

Field Volatility of Dicamba

Report: MRID 50020301. Jackson, S.H. 2016. Sampling for Possible Gaseous Field Loss after Application of a Commercial Herbicide (Summer Application). Unpublished study. Study performed, sponsored and submitted by BASF Crop Protection, Research Triangle Park, North Carolina. Study No.: 819375; BASF Registration Document No.: 2016/7009355. Study initiated June 7, 2016, and completed September 14, 2016 (pp. 5, 8). Final report issued September 14, 2016.

Document No.: MRID 50020301

Guideline: OCSPP 835.8100

Statements: This study was conducted according to the USEPA FIFRA Good Laboratory Practice (GLP) Standards (40 CFR Part 160), with the following exceptions (p. 3): the test substance used in the field phase of this study was a commercial product and was not characterized as required under GLP. The Exponent modeling report appended to this study is an evaluation of data after generation and was not conducted under GLP. Signed and dated Data Confidentiality, GLP Compliance, Quality Assurance, and Authenticity Certification statements were provided (pp. 2-5).

Classification: This study is Supplemental. Reported concentrations are based on nominal sampling period durations instead of actual sampling period durations. Less than half of laboratory spike samples are within the acceptable range. Application verification samples contained only 71% and 87% of the targeted applied amount of dicamba at Sites 1W and 2E, respectively. The soil matrix was not sampled. Estimated flux values with the indirect method are limited by few detects above the LOQ. The minimum fetch required for use of the aerodynamic method was not satisfied for all samplers. The initial air monitoring period did not start at the beginning of the application period, but instead started several minutes after the application period. An independent laboratory method validation was not conducted.

PC Code: 100094

**Final EPA
Reviewer:** William P. Eckel, Ph.D.

Signature:



Date: January 12, 2017

**CDM/CSS-
Dynamac JV
Reviewers:**

Richard R. Lester,
Environmental Scientist

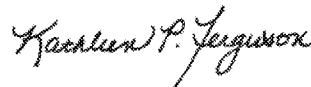
Signature:



Date: 12/15/16

Kathleen Ferguson, Ph.D.,
Environmental Scientist

Signature:



Date: 12/15/16

This Data Evaluation Record may have been altered by the Environmental Fate and Effects Division subsequent to signing by CDM/CSS-Dynamac JV personnel.

Executive Summary

Field volatilization of dicamba, formulation Engenia[®], a formulation containing 5 lb. a.e./gal, was examined from two cropped plots in Sumter County, Georgia. The sites where the studies were conducted were near Plains, Georgia. The experiments at these sites (Sites 1W and 2E) were conducted for approximately three days. The nominal application rate in the plot was 1 lb. a.e./A. The treated plots were approximately 1.75 km apart. No control plot was used, but untreated control sampling locations were located 55 m south of Site 1W and 55 m southwest of Site 2E.

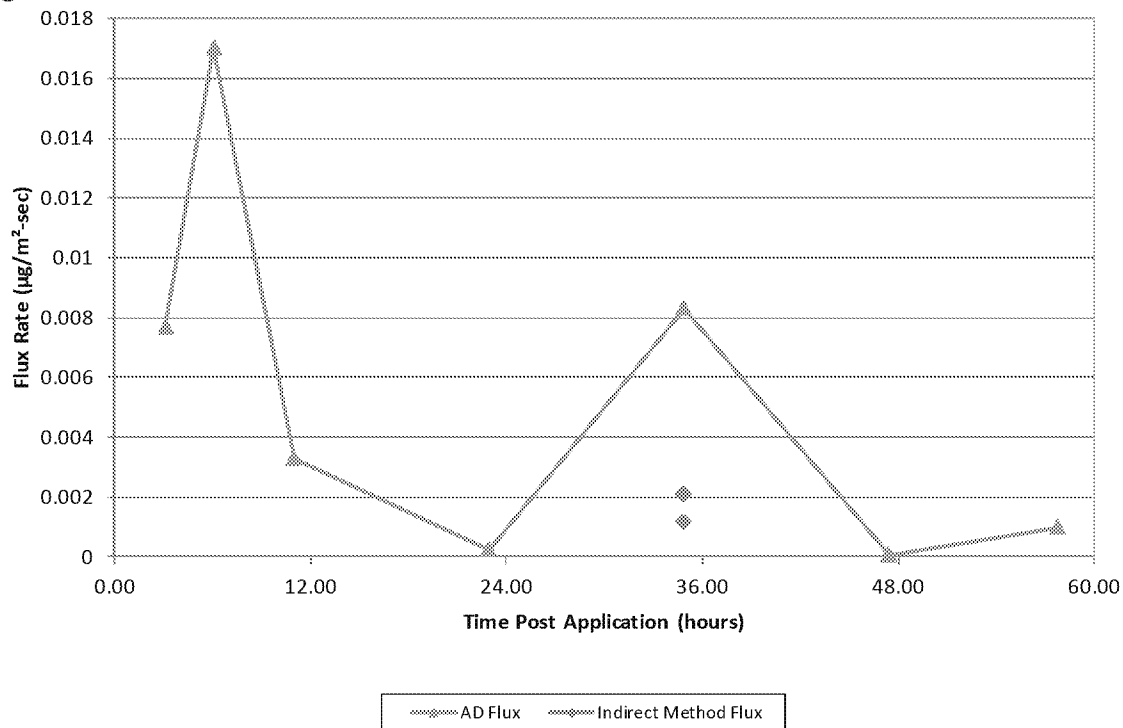
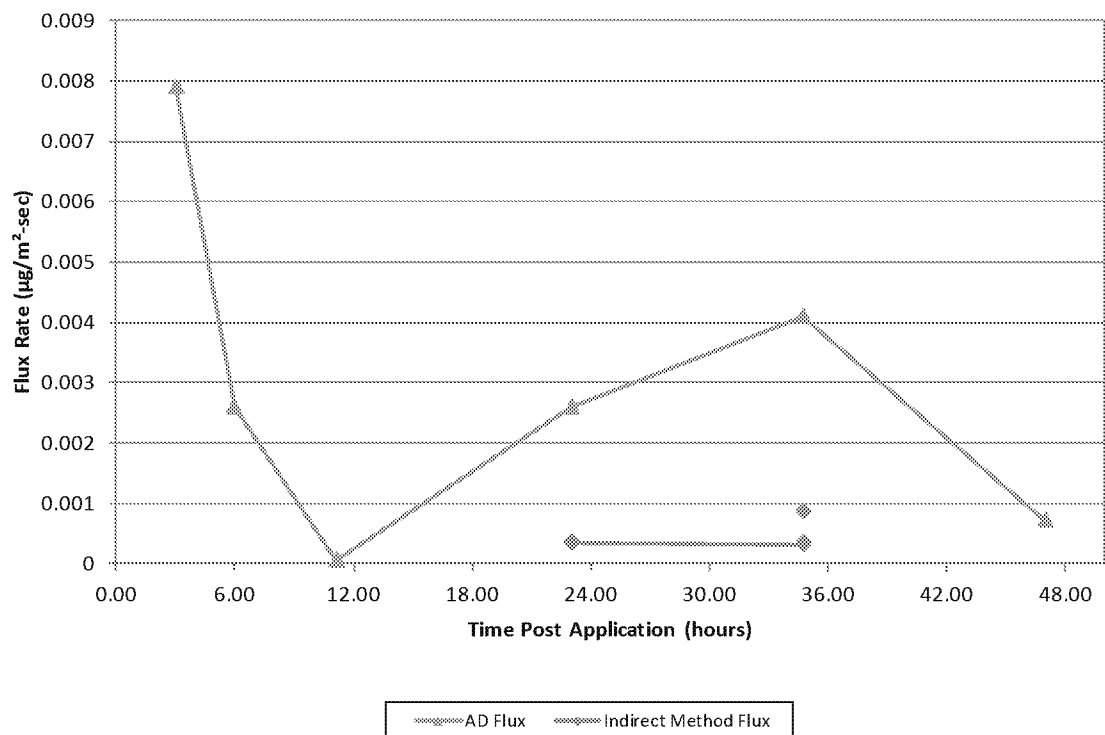
Under field conditions at Site 1W, based on calculations using the Aerodynamic method, a peak volatile flux rate of $0.017 \mu\text{g}/\text{m}^2\cdot\text{s}$ was measured accounting for 0.16%¹ of the applied observed 3 to 6 hours post-application. By the end of the study, a total of 0.64% of the applied dicamba volatilized and was lost from the field. A secondary peak volatile flux rate of $0.0083 \mu\text{g}/\text{m}^2\cdot\text{s}$ occurred at 24-36 hours post-application, during daytime hours the day after application.

Under field conditions at Site 1W, based on calculations using the Indirect method and very limited data, a peak volatile flux rate of $0.0021 \mu\text{g}/\text{m}^2\cdot\text{s}$ was estimated accounting for 0.080% of the applied observed 24 to 36 hours post-application. This is the only period for which volatile flux rates could be estimated using the Indirect method.

Under field conditions at Site 2E, based on calculations using the Aerodynamic method, a peak volatile flux rate of $0.0079 \mu\text{g}/\text{m}^2\cdot\text{s}$ was measured accounting for 0.071% of the applied observed 0 to 3 hours post-application. By the end of the study, a total of 0.38% of the applied dicamba volatilized and was lost from the field. A secondary peak volatile flux rate of $0.0041 \mu\text{g}/\text{m}^2\cdot\text{s}$ occurred at 24-26 hours post-application, during daytime hours the day after application.

Under field conditions at Site 2E, based on calculations using the Indirect method and very limited data, a peak volatile flux rate of $0.00087 \mu\text{g}/\text{m}^2\cdot\text{s}$ was estimated accounting for 0.032% of the applied observed 24 to 36 hours post-application. Volatile flux rates could only be estimated for the 12-24 hour and 24-36 hour periods post-application.

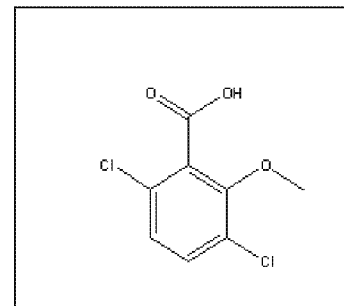
¹ All percentages of the amount applied are reviewer calculated based on the application rate and flux rates presented in MRID 50020301.

Figure 1. Dicamba Flux Rates for Site 1W**Figure 2. Dicamba Flux Rates for Site 2E**

I. Materials and Methods

A. Materials

- 1. Test Material** Product Name: Engenia[®] (p. 11)
Formulation Type: Liquid² (p. 12)
CAS #: 104040-79-1 (dicamba
BAPMA salt)
Storage stability: Not reported.



2. Storage Conditions

The test substance was stored at ambient temperature (5°C to 30°C) prior to the application (p. 37).

B. Study Design

1. Site Description

The test sites were located near the town of Plains, Sumter County, Georgia and were separated in distance by about 1.75 km (p. 12). The treated area at each test plot was approximately 120 m × 120 m. The test sites were uniform with respect to soil texture and vegetation and near uniform regarding slope with natural undulation present between 1% and 5% (p. 37). Agronomic and pesticide use history of both plots was documented for three years preceding the study (p. 40; Table 1, p. 44).

The test plot at Site 1W was located within a rectangular agricultural hay field measuring approximately 220 m × 440 m with a gradual diminishing slope from north to south (pp. 37-38). The crop was hay composed of Bermuda grass (*Cynodon* spp.) with a height of six to ten inches prior to application. The USDA taxonomic soil classification for the field is Norfolk loamy sand (p. 12).

The test plot at Site 2E was located within a trapezoidal agricultural hay field measuring 145 m wide at the north end, 265 m wide at the south end, 350 m long at the west end, and 290 m long at the east end (p. 38). The crop was hay composed of Bermuda grass (*Cynodon* spp.) with a height of six to ten inches. The USDA taxonomic soil classification for the field is Orangeburg loamy sand (p. 12).

2. Application Details

Application rate(s): The target application rate was 1.0 lb a.i./A (Table 2, p. 15). Based on swath pass times, swath distance, and the calibrated sprayer flow rate, the actual application rate was 1.03 lbs a.i./A for Site 1W and 1.02 lbs a.i./A for Site 2E (Table 2, p. 15). Application verification samples contained 71% and 87% of the target dicamba at Sites 1W and 2E, respectively (Table 20, p. 277).³

² The MRID quantifies the test material using units of volume (gallons) indicating a liquid formulation.

³ Reviewer calculated. Application verification samples contained 1,405 µg dicamba/sample and 1,725 µg

Irrigation and Water Seal(s): No irrigation water was used.

Tarp Applications: Tarps were not used.

Application Equipment: The applications were made with a tractor mounted 2016 Fimco 200 gallon PTO hydraulic sprayer equipped with a 24-foot boom (p. 40). The boom contained 17 nozzles spaced 18 inches apart, producing an effective spray swath of 25.5 feet. Turbo TeeJet Induction (TTI) 11005 nozzles were used per test substance label specifications. A pressure of 50 psi was selected based on manufacturer recommendations.

Equipment Calibration Procedures:

Sprayer calibration was performed by testing each nozzle and measuring the rate that liquid collected in a gallon bucket (pp. 40-41). Verification was conducted by spraying at 50 psi for 15 seconds. Nozzles were each tested three times to determine variability between nozzles and replication. The sprayer calibration established the output to be 7.1-GPM. Using the measured volume per minute output of the boom at 50 psi and a calibrated sprayer vehicle speed of approximately 5.6 mph in first gear, a spray rate of 25-GPA was achieved and set as the target spray rate.

Application Regime: The application rates and methods used in the study are summarized in **Table 1**.

Table 1. Summary of application methods and rates for dicamba

Site	Application Method	Time of Application (Date and Start Time)	Amount Dicamba Applied* (lbs)	Area Treated (acres)	Target Application Rate (lb ae/acre)	Reported Application Rate (lb ae/acre)
1W	Tractor-mounted broadcast spray	6/13/2016 11:07	3.67	3.56	1.0	1.03
2E	Tractor-mounted broadcast spray	6/13/2016 12:03	3.63	3.56	1.0	1.02

Data obtained from p. 41 and Table 3, p. 45.

*The amount of dicamba applied is reviewer calculated based on the treated area and reported application rates for each site.

Application Scheduling: Critical events of the study in relation to the application period are provided in **Table 2**.

dicamba/sample, respectively (Table 20, p. 277). Expected dicamba was 1983.3 µg/petri sample (Table 20, p. 277).

Table 2. Summary of dicamba application and monitoring schedule

Site	Treated Acres	Application Period	Initial Air/Flux Monitoring Period	Water Sealing Period	Tarp Covering Period
1W	3.56	06/13/16 between 11:07 – 11:20	06/13/16 between 11:44 – 14:27	Not Applicable	Not Applicable
2E	3.56	06/13/16 between 12:03 – 12:16	04/11/16 between 12:30 – 15:17	Not Applicable	Not Applicable

Data obtained from p. 41; Table 3, p. 45; and Table 1, p. 352.

3. Soil Properties

The soil matrix was not sampled in the study (pp. 12, 36). Known soil properties are provided in Table 3.

Table 3. Summary of soil properties for fields/plots

Site	Sampling Depth	USDA Soil Textural Classification	USGS Soil Series	WRB Soil Taxonomic Classification	Bulk Density (g/cm ³)	Soil Composition
1W	NA	NA	Norfolk loamy sand	NA	NA	NA
2E	NA	NA	Orangeburg loamy sand	NA	NA	NA

Data obtained from pp. 12, 36. NA indicates not applicable because the soil matrix was not sampled.

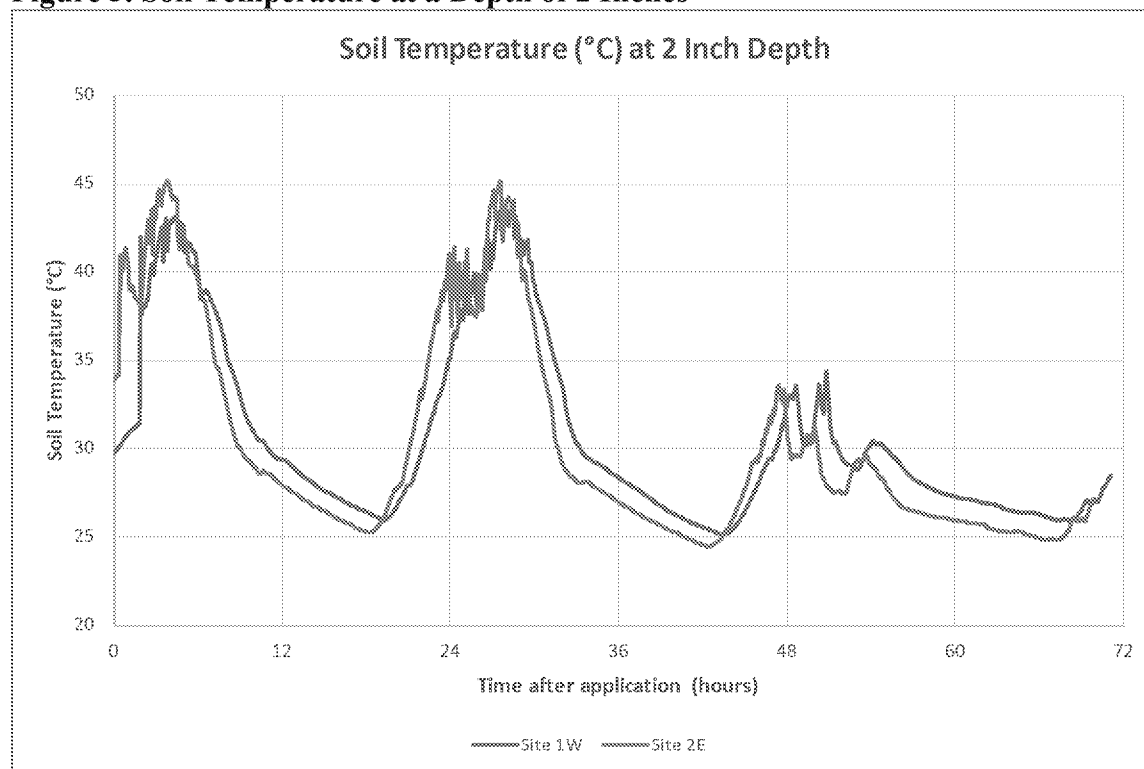
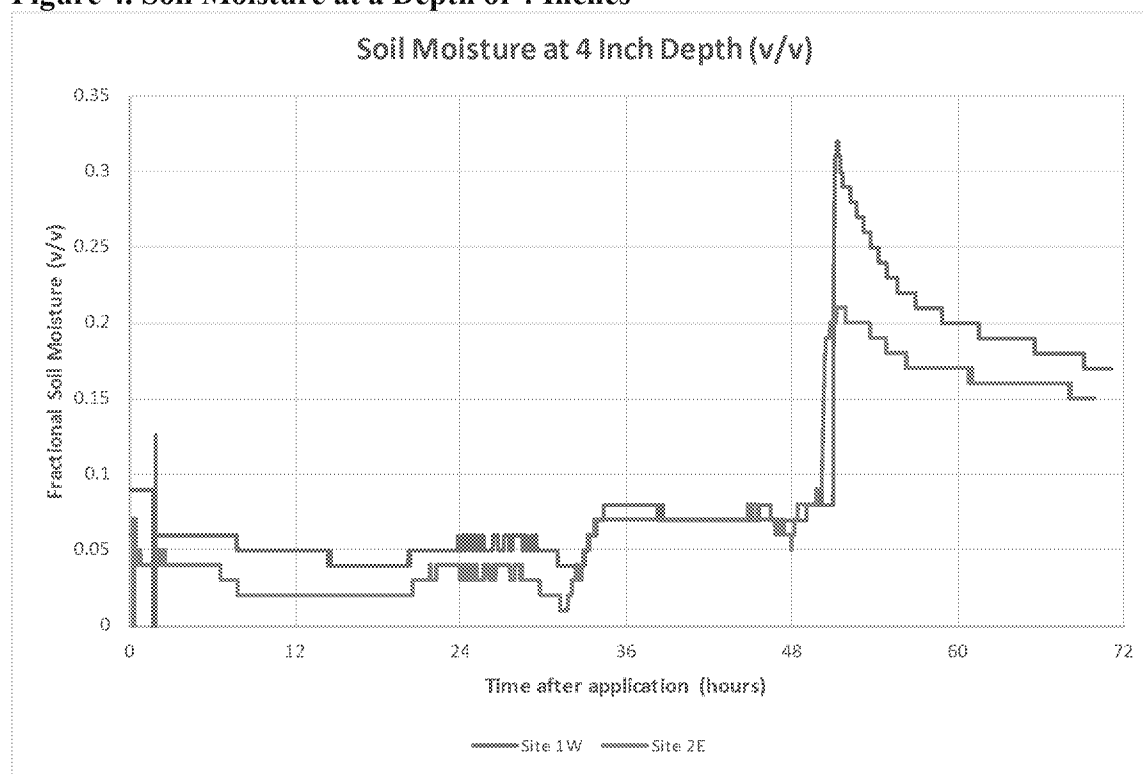
Figure 3. Soil Temperature at a Depth of 2 Inches

Figure 4. Soil Moisture at a Depth of 4 Inches

Soil temperature and soil moisture graphs are reviewer created from data on pp. 58-235.

4. Meteorological Sampling

Wind speed, wind direction, temperature, relative humidity, soil temperature and soil moisture were recorded at the test sites using on-site weather stations (pp. 14, 40). Weather parameters were measured at three heights above the vegetation (approximately 0.5 m, 1.0 m, and 1.5 m above the top of the vegetation). Soil temperature and soil moisture were measured at depths of two inches and four inches, respectively. The weather station at Site 1W was additionally equipped with a pyranometer for measuring solar radiation. A tipping bucket rain gauge for recording precipitation was attached to an independent fencing stake at a height of approximately 1.0 m above the top of the vegetation at each site. Weather station data were collected and stored on a 1-minute interval at both sites for the duration of the study.

One-minute weather data are included in an Appendix to the Final Field Phase Report (pp. 58-235).

The weather stations were deployed 15 m east of the plots near sampling station D prior to application and were then moved near the center of the plot (15 m east of sampling station I) immediately following application (p. 13).

Details of the sensor heights and the meteorological parameters for which data were collected are illustrated in Table 4. The location of the meteorological equipment for the plot is shown in Attachment 3.

Table 4. Summary of meteorological parameters measured in the field

Site	Minimum Fetch* (m)	Parameter	Monitoring heights (m)	Averaging Period
1W	64.3	Wind speed/Wind direction	0.5 m, 1.0 m, 1.5	1 minute
		Ambient air temperature	0.5 m, 1.0 m, 1.5	1 minute
		Relative humidity	0.5 m, 1.0 m, 1.5	1 minute
		Precipitation	1.0 m	1 minute
		Solar radiation	Not specified	1 minute
		Soil temperature	Depth 2 in	1 minute
		Soil moisture	Depth 4 in	1 minute
2E	65.9	Wind speed/Wind direction	0.5 m, 1.0 m, 1.5	1 minute
		Ambient air temperature	0.5 m, 1.0 m, 1.5	1 minute
		Relative humidity	0.5 m, 1.0 m, 1.5	1 minute
		Precipitation	1.0 m	1 minute
		Soil temperature	Depth 2 in	1 minute
		Soil moisture	Depth 4 in	1 minute

Data obtained from pp. 14, 40; and the Appendix to the Final Field Phase Report (pp. 58-235).

* Not reported in the MRID. Value indicated is the minimum average fetch for a sampling period. Values on a per minute basis are calculated in the accompanying spreadsheets.

5. Air Sampling

Ten PVC sampling masts were constructed for each test plot to hold active air sampler pumps and PUF/XAD tube sampling media (pp. 13-15, 38-40; Figures 1-3, pp. 49-51). Nine perimeter sampling locations were set up 15 m from the plot at the corners and mid-point of each side of the plot with sample tubes suspended at a height of 1.0 m above the hay. For the central plot sampling location, a modified sampling mast with five active air samplers and tubes was set up so that sampling occurred at heights of 0.2 m, 0.4 m, 0.6 m, 0.8 m, and 1.0 m above the hay. Untreated control sampling locations were set up 55 m south of the southwest corner of the treated area at Site 1W and 55 m southwest of the southwest corner of the treated area at Site 2E (p. 38). No pre-application samples were collected.

6. Sample Handling and Storage Stability

After collection, samples from sample periods 0-3 hour, 3-6 hour, and 6-12 hour were immediately placed in a freezer that was trailered to the site. Samples from other periods were placed into coolers with freezer packs at the test sites for temporary storage before being transferred to secure freezers at the field test facility, Harris Farms and Research (p. 42). Untreated control samples were handled and stored separately from other samples. Following termination of the field portion of the study, all PUF/XAD samples were packed in coolers with blue ice and driven from the field test facility to the analytical laboratory by the Principal Field Investigator (p. 43). All samples were checked into freezers at the analytical laboratory at 8:01 p.m. EDT on June 16, 2016. BASF has data which indicate the stability of dicamba residues on the involved matrix for more than 5 months (p. 23). The air sampling devices were stored frozen for no more than 23 days from collection to extraction for analysis (p. 23; Tables B.1-B.2, pp. 283-300). No corrections were made to account for instability.

7. Analytical Methodology

- Sampling Procedure and Trapping Material: Dicamba was monitored using PUF/XAD sample tubes (XAD-2 OVS quartz fiber 270/140 mg sorbent tubes, SKC Inc. Catalog No. 226-58A; p. 39) and SKC Leland Legacy[®] active air sampler pumps (SKC Inc. Catalog No. 100-3002). Plastic polytetrafluoroethylene (PTFE) tubing was used to connect pumps to samplers. The air pumps were set to draw 3 L per minute for the designated sampling periods (p. 18).
- Extraction method: A 10-ml portion of methanol/water (90:10, v/v) acidified with 1% formic acid was added to the OVS tube. Dicamba was extracted from the sorbent by mechanical shaking for 60 minutes at 300 rpm. The sample was removed from the shaker and allowed to settle for 2-5 minutes. A 1-mL aliquot was transferred to a clean culture tube and diluted with 3-mL of 1% formic acid in HPLC water. The sample was mixed by vortexing for about 10 seconds to dissolve any dicamba residue and then vialled for analysis by LC-MS/MS (p. 249; Figure C.1, p. 303).
- Method validation (Including LOD and LOQ): Method ADPEN M1407 “Technical Procedure: Analytical Method for the Determination of Residues of BAS 183 H (Dicamba) and Imazethapyr in OVS tubes with XAD-2 sorbent by LC-MS/MS” was used to analyze OVS tube samples (pp. 14-15, 241). The LOQ was 0.01 µg dicamba per sample, and the LOD was 0.002 µg per sample. This corresponds to an LOQ and LOD of 0.02 µg/m³ and 0.002 µg/m³, respectively, for a 3-hour sampling period and an LOQ and LOD of 0.005 µg/m³ and 0.0005 µg/m³ for a 12-hour sampling period (p. 354). No method validation activities are specified.
- Instrument performance: The performance of the instrument was evaluated during each injection set (pp. 249-250). The correlation coefficient for each calibration curve was no less than 0.99. Calibration standard concentrations for dicamba ranged from 0.025 to 10 ng/mL. Calibration curves were linear with 1/x weighting (pp. 249-250; Figure C.3, p. 305).

8. Quality Control for Air Sampling

Lab Recovery:	Less than half of laboratory spike recoveries are within the acceptable range of 90-110% following fortification at 0.01 (17 samples), 0.1 (15 samples), 0.3 (1 sample), and 1.0 µg/sample (1 sample) (Table 1, p. 258). Only 12 of 34 recoveries were within the acceptable range. Overall recoveries were between 71% and 124% with an average percent recovery (\pm RSD) of $91 \pm 13.4\%$. Samples outside the acceptable range include 10 of 17 samples at the fortification level of 0.01 µg/sample, 11 of 15 samples at 0.1 µg/sample, and the one sample at 1.0 µg/sample. Recoveries at the fortification level of 0.1 µg/sample were generally low, ranging from 71% to 98% with an average percent recovery (\pm RSD) of $84 \pm 9.6\%$.
Field blanks:	There was no dicamba measured in all untreated control samples collected from the two sites (Tables 3-18, pp. 260-275). ⁴
Field Recovery:	No field recovery is reported.

⁴ Table 7 (p. 264) indicates that dicamba was detected in the 24-36 hour untreated control sample from Site 1W; however, laboratory data reported for this sample indicate that this is an error in Table 7 with no dicamba detected in the untreated control sample (p. 325).

Travel Recovery: Mean recoveries of dicamba from five transit stability samples from each site fortified at 0.3 µg/sample were 89% at Site 1W (range from 77 to 98%) and 82% at Site 2E (range from 27 to 103%) (Table 19, p. 276). Excluding one outlier (a recovery of 27%), the range at Site 1W is 90 to 103% with a mean recovery of 96%.

Breakthrough: No explicit discussion of breakthrough is provided. Transit stability samples fortified at 0.3 µg/sample had an average recovery of 85.6% (Table 19, p. 276). The highest dicamba amount measured on a sample during the study was 0.195 µg/sample (Tables 3-18, pp. 260-275), indicating that dicamba loss due to breakthrough is unlikely.

9. Application Verification

Application verification samples collectors were placed within test plots prior to application (pp. 14, 40). The collectors were 150 mm petri dishes fitted with 150 mm filter paper trimmed to fit inside the petri dishes. Fifteen sample collectors were placed in each test plot in a line across the plot perpendicular to the direction of application. Petri dish covers were removed immediately prior to application and replaced immediately afterward. All application verification samples were placed in plastic bags and packed in coolers and then a separate freezer at the field test facility until transport to the lab for analysis (p. 42).

Petri dish samples appear to be composites of 14 petri dishes per field site (p. 255).⁵ The residue found for Site 1W was 1,405 µg/sample and for Site 2E was 1,725 µg/sample. Reviewer calculated recoveries for the two sites were 71% and 87%, respectively (theoretical amount of a.i. per petri dish (p. 277) 1,983.3 µg/sample).

Mean procedural recoveries of dicamba on petri dish samples was 116% (pp. 15, 241).

II. Results and Discussion

A. Empirical Flux Determination Method Description and Applicability

Flux modeling was determined using the aerodynamic method following the Thornthwaite-Holzman aerodynamic flux equation and by the indirect method following the CDPR methodology (p. 20; Appendix C, pp. 348-361).

Aerodynamic Method

The aerodynamic method, also referred to as the “flux-gradient” method, was the technique employed for estimating flux rates from fields treated for this field study given the available data. In the aerodynamic method, a mast is erected in the middle of the treated field and concentration samples are typically collected at four or five different heights, ranging from 0.5 to 10 feet. Likewise, temperature and wind speed data are collected at a variety of heights. A log-linear regression is performed relating the natural logarithm of the sample height to the concentration, temperature, and

⁵ It is unclear why only 14 of the 15 petri dish samples were included in the composite at each site.

wind speed. These relationships are then incorporated into an equation to estimate flux. The methods to estimate flux and related equations are presented in Majewski et al., 1990. The equation for estimating flux using the aerodynamic method is Thornthwaite-Holzman Equation, which is shown in the following expression:

$$\text{Equation } x_1 \quad P = \frac{k^2 (\Delta \bar{c})(\Delta \bar{u})}{\phi_m \phi_p \left[\ln \left(\frac{z_2}{z_1} \right) \right]^2}$$

where P is the flux in units of $\mu\text{g}/\text{m}^2 \cdot \text{s}$, k is the von Karman's constant (dimensionless ~ 0.4), $\Delta \bar{c}$ is the vertical gradient pesticide residue concentration in air in units of $\mu\text{g}/\text{m}^3$ between heights z_{top} and z_{bottom} in units of meters, $\Delta \bar{u}$ is the vertical gradient wind speed in units of m/s between heights z_{top} and z_{bottom} , and ϕ_m and ϕ_p are the momentum and vapor stability correction terms respectively.

Following the conditions expected in the neutrally stable internal boundary layer characterized by an absence of convective (buoyant) mixing but mechanical mixing due to wind shear and frictional drag, a log-linear regression is performed relating the natural logarithm of the sample height to the concentration, temperature, and wind speed. The adjusted values of the concentration, temperature, and wind speed from this regression is incorporated into Equation 2-1 to arrive at Equation 2-2 which is ultimately used to compute the flux.

$$\text{Equation } x_2 \quad \text{Flux} = \frac{-(0.42)^2 (c_{z_{\text{top}}} - c_{z_{\text{bottom}}})(u_{z_{\text{top}}} - u_{z_{\text{bottom}}})}{\phi_m \phi_p \ln \left(\frac{z_{\text{top}}}{z_{\text{bottom}}} \right)^2}$$

where ϕ_m and ϕ_p are internal boundary layer (IBL) stability correction terms determined according to the following conditions based on the calculation of the Richardson number, R_i :

$$\text{Equation } x_3 \quad R_i = \frac{(9.8)(z_{\text{top}} - z_{\text{bottom}})(T_{z_{\text{top}}} - T_{z_{\text{bottom}}})}{\left[\left(\frac{T_{z_{\text{top}}} + T_{z_{\text{bottom}}}}{2} \right) + 273.16 \right] + (u_{z_{\text{top}}} - u_{z_{\text{bottom}}})^2}$$

where $T_{z_{\text{top}}}$ and $T_{z_{\text{bottom}}}$ are the regressed temperatures at the top and bottom of the vertical profile in units of $^{\circ}\text{C}$.

if $R_i > 0$ (for Stagnant/Stable IBL)

$$\phi_m = (1 + 16R_i)^{0.33} \text{ and } \phi_p = 0.885(1 + 34R_i)^{0.4}$$

if $R_i < 0$ (for Convective/Unstable IBL)

$$\phi_m = (1 - 16R_i)^{-0.33} \text{ and } \phi_p = 0.885(1 - 22R_i)^{-0.4}$$

The minimum fetch requirement that the fetch is 100 times the highest height of the air sampler for this method to be valid [was/was not] satisfied at all times [List the sampling periods and resulting fetches with exceptions]. The aerodynamic method used to estimate flux and related equations are presented in Majewski et al., 1990.

Indirect Method

The indirect method, commonly referred to as the “back calculation” method, was the technique employed for estimating flux rates from fields treated for this field study given the available data. In the indirect method, air samples are collected at various locations outside the boundaries of a treated field. Meteorological conditions, including air temperature, wind speed, and wind direction, are also collected for the duration of the sampling event. The dimensions and orientation of the treated field, the location of the samplers, and the meteorological information are used in combination with the ISCST3 dispersion model (Version 02035) and a unit flux rate of $0.001 \mu\text{g}/\text{m}^2\cdot\text{s}$ to estimate concentrations at the sampler locations. Since there is a linear relationship between flux and the concentration at a given location, the results from the ISC model runs are compared to those concentrations actually measured, and a regression is performed, using the modeled values along the x-axis and the measured values along the y-axis. If the linear regression does not result in a statistically significant relationship, the regression may be rerun forcing the intercept through the origin, or the ratio of averages between the monitored to modeled concentrations may be computed, removing the spatial relationship of the concentrations. The indirect method flux back calculation procedure is described in detail in Johnson et al., 1999.

B. Temporal Flux Profile

The flux determined from the registrant and reviewer for each sampling period after the application is provided in **Tables 5** and **6**.

Table 5. Field volatilization flux rates of dicamba obtained in study [Site 1W]

Sampling Period	Date/ Time	Sampling Duration (hours)	Flux Estimate			
			Reviewer ($\mu\text{g}/\text{m}^2\text{-sec}$)	Registrant ($\mu\text{g}/\text{m}^2\text{-sec}$)	Empirical Flux Determination Method ¹	Notes
1	06/13/16 11:44 – 14:27	2.72		0.0077	AD	
2	06/13/16 14:30 – 17:24	2.90		0.017	AD	
3	06/13/16 17:28 – 22:18	4.83		0.0033	AD	
4	06/13/16 22:22 – 06/14/16 10:16	11.90		0.00025	AD	
5	06/14/16 10:20 – 22:11	11.85		0.0083 0.0021 & 0.0012	AD ID	
6	06/14/16 22:30 – 06/15/16 10:46	12.27		0.000073	AD	
7	06/15/16 10:51 – 21:07	10.27		0.00098	AD	
8	06/15/16 21:13 – 06/16/16 9:24	12.18				2

Data obtained from Table 1, pp. 352-353; Table 9, p. 358; and Table 11, p. 361 in the study report.

¹ Methods legend: AD = Aerodynamic Method, ID = Indirect Method.

² Dicamba was not detected sufficiently frequently to determine flux estimates during sampling period 8.

Table 6. Field volatilization flux rates of dicamba obtained in study [Site 2E]

Sampling Period	Date/ Time	Sampling Duration (hours)	Flux Estimate			
			Reviewer ($\mu\text{g}/\text{m}^2\text{-sec}$)	Registrant ($\mu\text{g}/\text{m}^2\text{-sec}$)	Empirical Flux Determination Method ¹	Notes
1	06/13/16 12:30 – 15:17	2.78		0.0079	AD	
2	06/13/16 15:22 – 18:15	2.88		0.0026	AD	
3	06/13/16 18:20 – 23:23	5.05		0.000062	AD	
4	06/13/16 23:27 – 06/14/16 11:16	11.82		0.0026 0.00035	AD ID	
5	06/14/16 11:22 – 22:59	11.62		0.0041 0.00087, 0.00033, & 0.00036	AD ID	
6	06/14/16 23:06 – 06/15/16 11:15	12.15		0.00073	AD	
7	06/15/16 11:19 – 21:43	10.40				2
8	06/15/16 21:48 – 06/16/16 09:45	11.95				2

Data obtained from Table 2, pp. 353-354; Table 10, p. 359; and Table 11, p. 361 in the study report.

¹ Methods legend: AD = Aerodynamic Method, ID = Indirect Method.

² Dicamba was not detected sufficiently frequently to determine flux estimates during sampling periods 7 and 8.

Maximum volatile flux rates occurred during sampling periods 1 or 2 shortly after application. A secondary peak flux rate occurred during sampling period 5, during the warm daytime hours the day after application. Dicamba was not detected above the LOQ during sampling period 8 at Site 1W and during sampling periods 7 and 8 at Site 2E; hence, the flux was not estimated for these periods.

Regression coefficients relating concentration, wind speed, and temperature to height were predominantly statistically significant, though the correlation coefficients varied (p. 355). For Site 1W, the r^2 values for concentration and height ranged from 0.68 to >0.99. For wind speed, the r^2 values were 0.99 or greater. For temperatures, the r^2 values of the regressions ranged from 0.57 to >0.99. The low value of 0.57 occurred during the 6-12 hour period; all other r^2 values were 0.93 or higher.

For Site 2E, the r^2 values for concentration and height ranged from 0.12 to 0.94. The low value of 0.12 was for the 3-6 hour period. For wind speed, the regressions for Site 2E were 0.10 to 0.97. The two low values of 0.10 were the result of the wind speed at 150 cm being lower than the wind speed at 100 cm. For temperatures, the r^2 values of the regressions ranged from 0.56 to 0.97 (p. 356).

Limited quantified residues at offsite monitors significantly limited the analysis using the indirect method. There were two detects above the LOQ at Site 1W and four detects at Site 2E. A simplified approach was used where the flux was estimated as the ratio of the measured air concentration and predicted air concentration multiplied by the nominal flux of 10^{-6} g/m²-sec (pp. 360-361).

III. Study Deficiencies and Reviewer's Comments

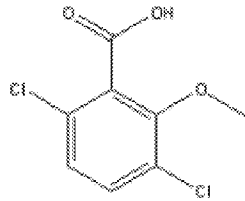
1. The dicamba concentrations reported in Table 1 (pp. 352-353) are based on the nominal sampling period duration (3, 6, or 12 hours) instead of the actual sampling period duration.
2. The dicamba concentration data summarized in Table 5 (p. 19) and Table 7 (p. 264) for the 24-36 hour sample are incorrect based on the laboratory data (p. 325).
3. Less than half of the laboratory spike samples are within the acceptable range of 90-110%
4. At site 1W, all data collected from the 0.8 m sampling height are non-detects while 1.0 m data have detects during the first five sampling periods, suggesting a possible issue with one of the samplers.
5. Based on reviewer calculations, the application verification samples contained only 71% and 87% of the targeted amount of dicamba applied at Sites 1W and 2E, respectively.
6. The soil matrix was not sampled. Soil bulk density and organic matter content were not reported.
7. Negative values are reported for several soil moisture measurements (pp. 72 and 159).
8. The minimum fetch required for use of the aerodynamic method was not satisfied for the samplers positioned at 0.8 and 1.0 meters above the hay.
9. A control sample was collected upwind of each site, but no untreated replicate subplot was established.
10. Field spiked samples were not deployed.
11. No independent analytical method validation was performed. A method validation study should be completed from an independent laboratory separate from and prior to the analysis of the test samples to verify the analytical methods.
12. Storage stability of the test material was not provided. Information about the stability of dicamba residues on the sampling matrix was provided.
13. The initial air monitoring period did not start at the beginning of the application period, but instead started 24 minutes (Site 1W) and 14 minutes (Site 2E) after the application period.
14. No pre-application samples were collected.

15. The test plot was not irrigated though precipitation occurred during the study. The study design should include irrigation according to the label requirements.
16. Wind speed and temperature measurements were reported in units of mph and °F instead of m/s and °C.

IV. References

- Johnson, B., Barry, T., and Wofford P. 1999. Workbook for Gaussian Modeling Analysis of Air Concentrations Measurements. State of California Environmental Protection Agency, Department of Pesticide Regulation. Sacramento, CA.
- Majewski, M.S., Glotfelty, D.E., Kyaw Tha Paw U., Seiber, JN. 1990. A field comparison of several methods for measuring pesticide evaporation rates from soil. *Environmental Science and Technology*, 24:1490-1497.
- Wilson, J.D., and Shum. W.K.N. 1992. A re-examination of the integrated horizontal flux method for estimating volatilisation from circular plots. *Agriculture Forest Meteor.* Vol 57:281-295.
- Yates, S.R., F.F. Ernst, J. Gan, F. Gao, and Yates, M.V. 1996. Methyl Bromide Emissions from a Covered Field: II. Volatilization," *Journal of Environmental Quality*, 25: 192-202.

Attachment 1: Chemical Names and Structures

Code Name/ Synonym	Chemical Name	Chemical Structure
PARENT		
Engenia® Herbicide/ Dicamba as the BAPMA salt	IUPAC: 3,6-Dichloro- <i>o</i> -anisic acid, BAPMA salt CAS: 3,6-Dichloro-2- methoxybenzoic acid, BAPMA salt CAS No.: 104040-79-1 Formula: C ₈ H ₆ Cl ₂ O ₃ MW: 221.04 g/mol SMILES String: <chem>CLc1ccc(CL)c(OC)c1C(=O)(O)</chem>	

Attachment 2: Statistics Spreadsheets and Graphs

[Insert supporting electronic spreadsheet files here (electronic attachment files are electronically finalized as separate files as well). Name electronic attachments the same file name as the Microsoft Word study review file with the addition of “Calc” for Excel workbooks and WinZip files, the addition of “Data” for Adobe Acrobat and Document Imaging files, and the addition of brief descriptors as appropriate for SigmaPlot Notebooks. Compress electronic attachment files into a WinZip file when three or more are prepared for a study review.]

[Print hard copies of the study review and any attachment sheets from separate electronic files to produce one hard copy file for finalization.]

[Example Excel files and spreadsheets follow below.]

1. Validation spreadsheet for studies following the Indirect Method:



Indirect Method.xlsx

2. Validation spreadsheet for studies following the Aerodynamic Method:



Aerodynamic
Method.xlsx

Attachment 3: Field Volatility Study Design and Plot Maps

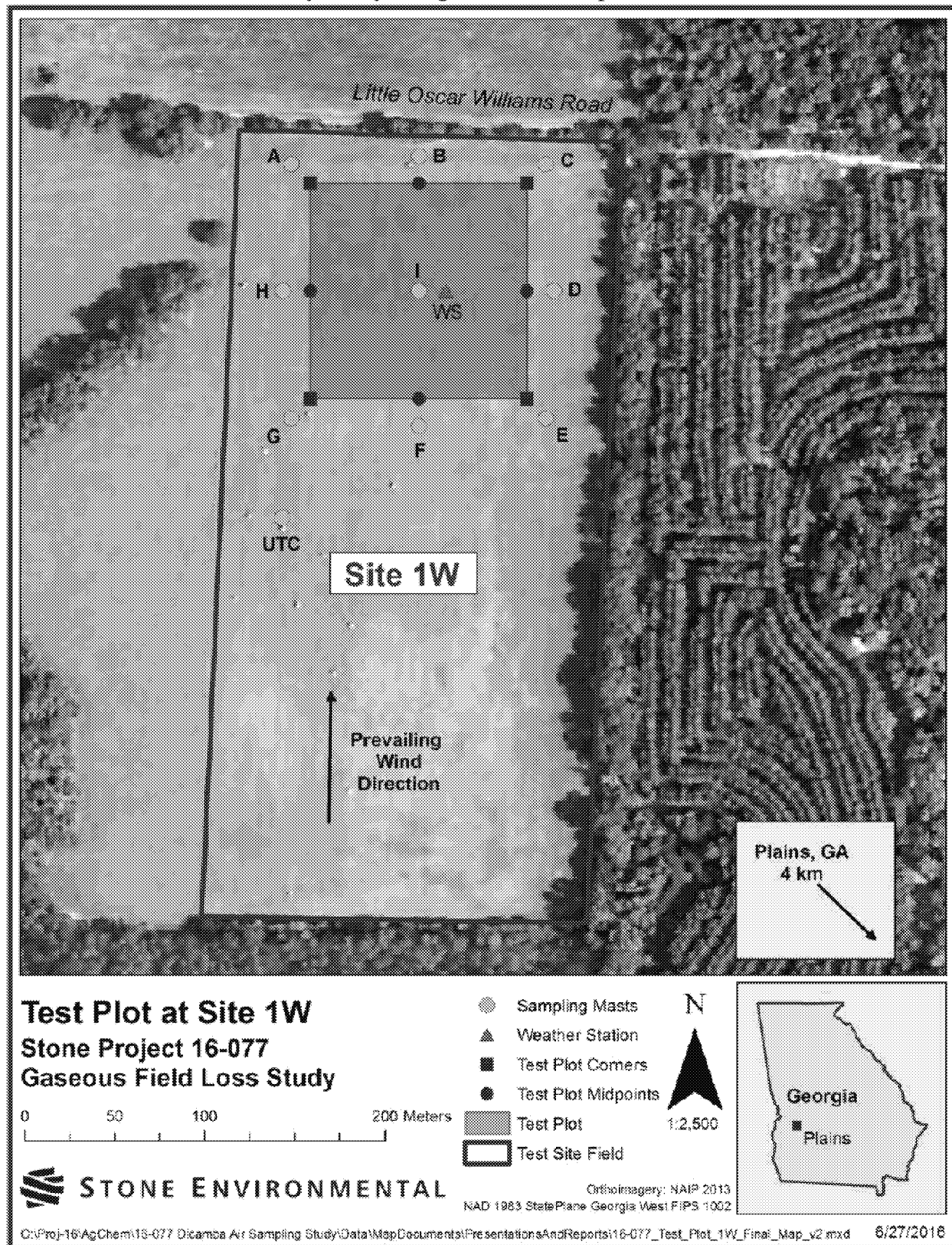


Figure obtained from Figure 2, p. 50 of the study report.

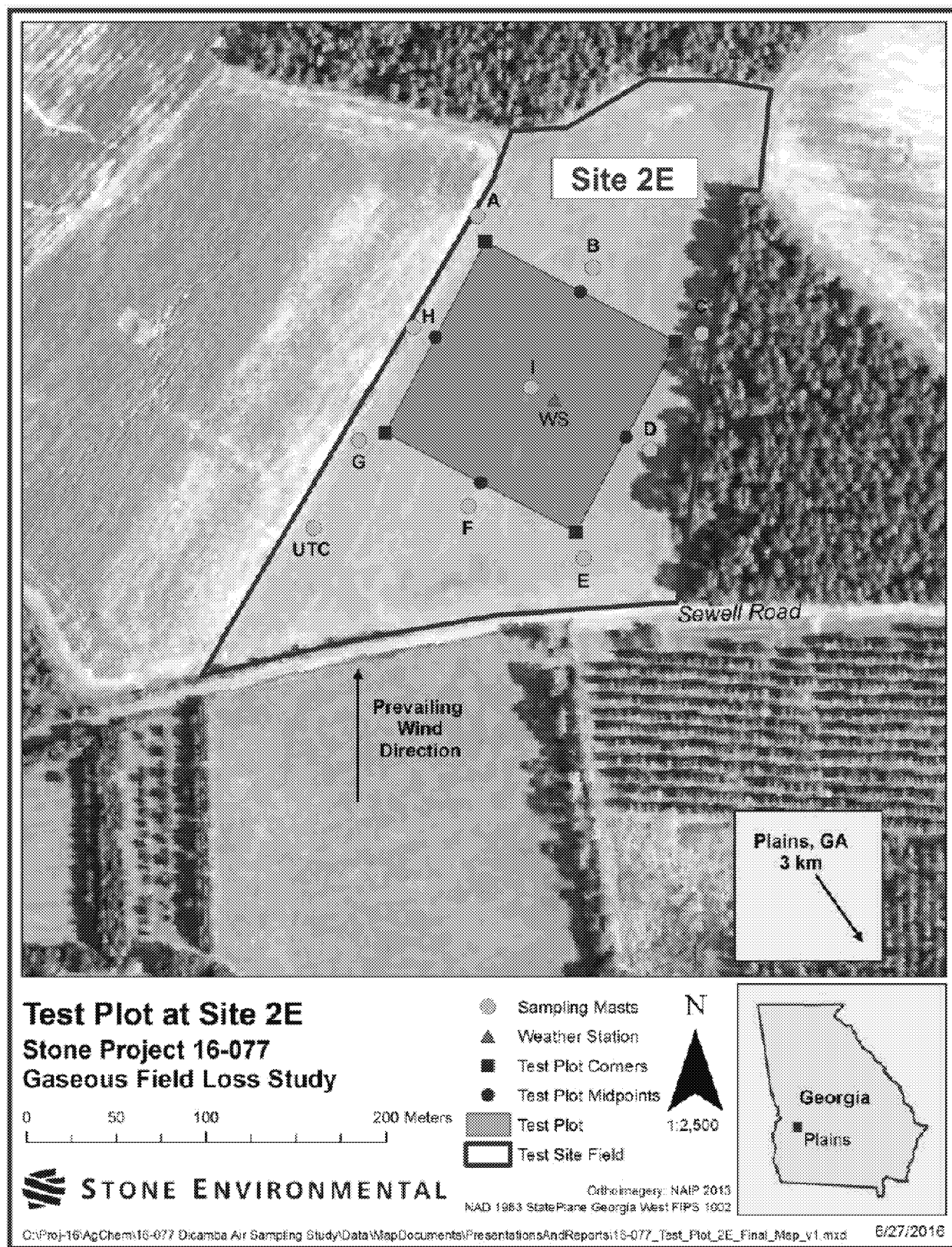


Figure obtained from Figure 3, p. 51 of the study report.

Attachment 4: Calculations and Index of Variables Used in Flux Determination Methods*Aerodynamic Method*

$$\text{Equation x}_1 \quad \text{Flux} = \frac{-(0.42)^2 (c_{z_{top}} - c_{z_{bottom}})(u_{z_{top}} - u_{z_{bottom}})}{\phi_m \phi_p \ln\left(\frac{z_{top}}{z_{bottom}}\right)^2}$$

Flux ($\mu\text{g}/\text{m}^2\text{s}$): volatile flux of pesticide from release source surface

$c_{z_{top}}$ ($\mu\text{g}/\text{m}^3$): concentration at the top sampler adjusted according to the regression of concentration vs. \ln (height)

$c_{z_{bottom}}$ ($\mu\text{g}/\text{m}^3$): concentration at the bottom sampler adjusted according to the regression of concentration vs. \ln (height)

$u_{z_{top}}$ (m/s): wind speed at the top sampler adjust according to the regression of wind speed vs. \ln (height)

$u_{z_{bottom}}$ (m/s): wind speed at the top sampler adjust according to the regression of wind speed vs. \ln (height)

ϕ_m and ϕ_p (dimensionless): Internal Boundary Layer (IBL) stability correction terms determined according to the following conditions based on the calculation of the Richardson number, R_i :

$$\text{Equation x}_2 \quad R_i = \frac{(9.8)(z_{top} - z_{bottom})(T_{z_{top}} - T_{z_{bottom}})}{\left[\left(\frac{T_{z_{top}} + T_{z_{bottom}}}{2}\right) + 273.16\right] + (u_{z_{top}} - u_{z_{bottom}})^2}$$

where:

$T_{z_{top}}$: Temperature at the top sampler adjusted according to the regression of temperature vs. \ln (height)

$T_{z_{bottom}}$: Temperature at the bottom sampler adjusted according to the regression of temperature vs. \ln (height)

R_i (dimensionless): Richardson Number

if $R_i > 0$ (for Stagnant/Stable IBL)

$$\phi_m = (1 + 16R_i)^{0.33} \text{ and } \phi_p = 0.885(1 + 34R_i)^{0.4}$$

if $R_i < 0$ (for Convective/Unstable IBL)

$$\phi_m = (1 - 16R_i)^{-0.33} \text{ and } \phi_p = 0.885(1 - 22R_i)^{-0.4}$$